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RESEARCH IN THE CHEMICAL, PHYSICAL, AND METALLURGICAL SCIENCES, TASKS 1, 3, AND 4

APRIL 1963

COMMANDER

AIR FORCE FLIGHT TEST CENTER

ATTENTION: DGPC

EDWARDS AIR FORCE BASE, CALIFORNIA

PROJECT NO. 3850

TASK NO. 385004

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RESEARCH IN THE CHEMICAL,
PHYSICAL, AND METALLURGICAL SCIENCES
TASKS I, 3, AND 4

April 1963

Commander
Air Force Flight Test Center
Attention: DGPC
Edwards Air Force Base, California

Project No. 3850
Task No. 385004
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FOREWORD

The work described in this report was carried out in partial fulfillment of Contract No. AF04(611)-8502, and covers the period 25 December 1962 to 25 March 1963. The program consists of four tasks. This report, however, deals only with Tasks 1,3, and 4. Task 2, which deals with deliverable equipment, is to be described fully in a special task report within the contract period.

The responsible engineer for this program is Mr. E.F.C. Cain, Group Scientist, Engineering and Analytical Chemistry Group. Administration and technical direction of the program was performed by Dr. B. L. Tuffly, Principal Scientist, Analytical Chemistry Unit. Work on the several tasks was coordinated by Mr. R. E. Bell.

The technical investigations for the various tasks were performed by:

    Task 1 - Dr. H. G. Offner, Principal Investigator
            Dr. V. Dayan

    Task 3 - Mr. I. Lysyj, Principal Investigator
            P. Newton
            B. Neale
            G. Brull

    Task 4 - Dr. R. C. Greenough, Principal Investigator
            D. V. Owens

ABSTRACT

TASK 1 - A number of plastic films were tested, but none were found sufficiently permeable to provide a sensitive and practical sensing device. A new method is proposed to convert pentaborane to hydrogen, which may then be sensed with the membrane electrode. The experimental work is now in progress on the rapid and quantitative conversion of pentaborane to hydrogen.

TASK 2 - A reliability and performance study was conducted using a hydrogen analyzer in conjunction with a Cosmodyne CS-4.4 cryogenic sampler. A mixture of Ne and He was separated on a 20-foot long molecular sieve 5A column held at approximately -78C, using hydrogen gas as the carrier. In the study dealing with cryogenic fluorine, characterization and optimization of the monophase gel column was attempted. The quantitative approach for the determination of particulate matter in liquids using the device described in the previous report was attempted using $Al_2 O_3$ powder and Al suspended in water.

TASK 3 - The composition of the samples of firing residues under investigation has now been explained. Borazole and, subsequently, poly-borazole have been synthesized, and the latter has been subjected to elemental analysis.

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ILLUSTRATIONS

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INTRODUCTION

This program is directed toward advancing the state of the art of
analytical chemistry as applied to rocket propellants. Specific task
efforts discussed in this report include: (1) development of a fast-
responding, highly sensitive detector for electroactive materials in
gases and liquids; (2) development of techniques for chemical analysis of
cryogenic materials; and (3) establishment of the chemical structure of
pentaborane-hydrazine firing residues.

This is the second special report under Contract AF04(611)-8502 and
will be followed by a final report.

TASK 1

FEASIBILITY STUDIES OF THE POLAROGRAPHIC MEMBRANE

H. G. Offner, Principal Investigator

V. Dayan

INTRODUCTION

Oxygen determinations using galvanic systems have been used successfully in gas streams. Hersch (Ref. 1) and Baker et al (Ref. 2) reported systems consisting of a silver cathode and a lead anode immersed in 24 weight percent potassium hydroxide, and Keidel (Ref. 3) also developed a sensitive instrument for trace quantities of oxygen based on a silver-cadmium galvanic couple. Other systems based on electrochemical reactions have been used to monitor gas streams for various impurities. In all cases, one of the principal problems has been the effect of electroactive or surface active impurities which either react with or poison the sensing device. One way to avoid the effect of such impurities is to scrub the gas before moving it to the sensing electrode. Another and simpler approach is to cover the electrode with a membrane permeable to oxygen and nonpermeable to other substances.

Clark et al (Ref. 4) described a procedure for measuring dissolved oxygen using a polyethylene-covered platinum electrode. Sawyer et al (Ref. 5) studied different kinds of Teflon and polyethylene membranes for the quantitative measurement of oxygen and sulfur dioxide in gas mixtures. This membrane electrode has been developed commercially by Beckman Instruments Corporation for the quantitative measurement of oxygen concentrations in gases to 100 ppm and in liquids to less than 1 ppm. D. A. Okum et al (Ref. 6) describe an improved version of this electrode system. The membrane electrode closely approaches such desired characteristics of a monitoring device as stability, ruggedness, simplicity, and selectivity. The detailed theory and advantages of this detection system have been described in previous reports.

SUMMARY

This report presents a feasibility study on the use of a membrane electrode for the detection and measurement of pentaborane in air. A number of plastic films were tested, but none were found sufficiently permeable to provide a sensitive and practical sensing device.

A new method is proposed to convert pentaborane to hydrogen, which may then be sensed with the membrane electrode. Experimental data are presented to demonstrate that this method affords adequate sensitivity and retains all the advantages of the membrane electrode principle. The experimental work is now in progress on the rapid and quantitative conversion of pentaborane to hydrogen.

DISCUSSION

The present study was initiated to develop instruments for the measurement of fuels and oxidizers (e.g., pentaborane and oxygen difluoride) in air and liquids at low concentrations. Thus far, only the case of pentaborane has been under investigation, chiefly because the problem has remained unsolved. The present device, the Olin-Mathieson "Demon" detector, has proved unsatisfactory because the exposed electrode is susceptible to contamination and poisoning; it also responds to many other air contaminants which may be present with the pentaborane. The nature of this problem suggested the use of selective plastic-membrane covered electrode for monitoring pentaborane in both gases and liquids.

A number of plastic films commercially available and one film specially prepared (denitrated collodion) have been tested in this study. No particular guiding principle was used in selecting the materials tested, and undoubtedly the list is not exhaustive. Membrane technology is not sufficiently advanced to permit definite predictions of permeability to various vapors. However, certain general principles are known. The size of the gas molecule is one factor determining the rate at which a gas diffuses in elastomers. Helium (diameter 1.9 $\overset{o}{A}$) diffuses three to four times as fast as hydrogen (diameter 2.4 $\overset{o}{A}$) in various synthetic materials. Oxygen, nitrogen, and carbon dioxide, with molecular diameters of approximately 3.0, 3.1, and 3.4 $\overset{o}{A}$, respectively, show still lower diffusivities, as might be expected (Ref. 7). Although data on the size of the pentaborane molecule were not available, it is undoubtedly larger than these molecules and therefore would permeate a given membrane at a slower rate. It would also be predicted on the basis of molecular size, and has in fact been determined experimentally (Ref. 7), that the ratios of the permeability of a given membrane to various gases are nearly the same for all other membranes. Therefore, it is possible to predict qualitatively the permeability of a barrier to

one gas when its permeability to another gas is known. The permeability of various plastic films to hydrogen has been measured, and a few values are shown in Table 1. The permeability constant is a function of the diffusion rate.

TABLE 1

HYDROGEN PERMEABILITIES

Film	Permeability Constant to Hydrogen, 25C (Ref. 7)
Polyethylene	0.82
Mylar	0.06
Nylon	0.03
Cellulose Acetate	0.80
Cellulose Acetate Butyrate	2.10

A number of compositional and structural variables of polymers affect their permeabilities; therefore, these values vary widely for a given material, depending on the manufacturing process. However, of all the various samples for each material tested, none approached the permeability of cellulose acetate butyrate. This material was also found to be most permeable to pentaborane.

Another complication in predicting permeabilities is that mixed gases do not always permeate independently of each other. Swelling due to water absorption increases permeability in the case of cellulose plastics. Similarly, oxygen permeates polyethylene at rates up to three times as fast in the presence of large amounts of carbon dioxide because of solution and swelling of the membrane by the carbon dioxide.

RESULTS

Table 2 summarizes the experimental results. The Beckman platinum-
membrane electrode was used for all measurements. A potential of +0.4
volts vs the silver-silver chloride electrode was applied to the plati-
num anode. The electrolyte was either an acid carbitol or an acid
methanol solution. Both of these solvents will hydrolyze pentaborane
to form hydrogen, which is then oxidized at the polarized platinum
electrode, causing a current flow. Alternately, the pentaborane itself
may be oxidized at the platinum surface. The data were obtained using
a 0.5-percent mixture of pentaborane in helium.

The response values were not reduced permeability values, since the mag-
nitude of the response with the available films, not permeability con-
stants, were of interest. Also, the time required to obtain a certain
fraction (e.g., 0.9) of the maximum response was not recorded because,
although considerably less than the maximum time in some cases, it is
this latter value which is of interest for quantitative measurements.

Several problems were encountered making the above measurements. Many
materials seemed to have pinholes which greatly increased the magnitude
of the signal for certain samples. Other membranes, such as the de-
nitrated collodion, goldbeaters skin, and gelled cellophane, were so
fragile that it was difficult to stretch them across the electrode with-
out tearing. Another difficulty causing erratic results was the variation
in resistance of the galvanic cell from run to run. Small differences in
the tension of the membranes against the platinum surface would cause
wide variations in these resistance values and subsequent fluctuations
in the observed current. The values shown in Table 2 are the maximum
values observed.

Because the results of the experiments indicate intolerably long response
times and low sensitivities, it was decided that the direct determination
of pentaborane with the membrane electrode is not feasible.

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TABLE 2

COMPARATIVE PERMEABILITIES OF VARIOUS FILMS TO PENTABORANE

Membrane Material	Thickness, mils	Response, microamps	Response, microamps/ppm x 10^3	Time required for maximum signal, minutes
Cellulose acetate butyrate	1.1	9	1.8	4
Cellulose butyrate	1.0	1	0.2	6
Teflon (Kel-F plasticized)	0.5	0	-	-
Teflon (Kel-F plasticized)	1.0	0	-	-
Teflon (FEP)	0.5	0	-	-
Polypropylene	0.5	0	-	-
Polystyrene	1.0	0	0	-
Silicone rubber	12.0	0	-	-
Denitrated collodion	2.1	2	0.4	3
Polyethylene*	1.0	2	0.1	2
Gelled cellophane*	2.0	26	1.7	4
Osmotic cellophane*	1.0	22	1.5	4
Unsized cellophane*	1.0	29	1.9	8
Teflon*	1.0	0	-	-
Goldbeaters Skin*	0.4	16	1.1	5
Mylar*	0.5	0	-	-
Saran*	0.5	0	-	-

*Tested using 1.47-percent pentaborane in helium mixture.

The use of microporous membranes was also contemplated, and several experimental runs were made using these films over the platinum electrode. Both cellulose-type materials, such as the millipore-type filters, and polyethylene films having discrete pore sizes in the micron range, were used. These materials are fragile and very difficult to tighten over the platinum electrode. Furthermore, while several of these films proved permeable to pentaborane, they are probably insufficiently nonpermeable to other contaminant gases which could poison the platinum electrode. Therefore, there is little difference between this type of electrode and the exposed platinum electrode on the monitor presently used. Some work was carried out on the development of a porous carbon electrode. A hollow electrode was fabricated from porous carbon. This cylinder was then impregnated with platinic acid from which platinum was deposited electrolytically. High sensitivities to pentaborane were obtained with this system, but it suffers from the same disadvantages as the exposed platinum electrode. Therefore, this approach was abandoned.

Because of the negative results of previous attempts to use the membrane electrode for the direct determination of pentaborane in air, a different experimental technique was devised. Hydrogen has a very high diffusivity in most membrane materials, and pentaborane can be hydrolyzed easily to boric acid and hydrogen under the proper conditions. Therefore, it should be possible to convert pentaborane to hydrogen by passing it through a suitable reagent and to detect the hydrogen with the membrane electrode. This system would sacrifice some simplicity in construction, since a pump is required to move the gas through the system. All of the advantages of the membrane electrode, however, would be retained.

The sensitivity of the Beckman membrane electrode to hydrogen was determined with various mixtures of hydrogen in nitrogen at concentrations determined by calculation from the measured flowrates of the two gas streams. A 10-percent potassium chloride solution was used for the electrolyte, and no external potential was applied between the platinum anode and the silver-silver chloride electrode, because the +0.2V of the reference half cell is sufficient to oxidize the hydrogen gas at the bright platinum electrode. The results are shown in Table 3. A 1-mil Teflon film was used for the membrane.

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TABLE 3

SENSITIVITY OF A MEMBRANE ELECTRODE TO HYDROGEN GAS

Hydrogen Concentration, mg/1000 gms	Response, microamps	Microamps/ x 10^3 ppm H_2
394	2.5	6.4
946	6.0	6.3
1740	9.8	5.6
4060	16.0	2.5
7440	29.0	3.8
11,500	40.0	3.5
15,700	48.4	3.1

The maximum current is obtained 10 seconds after exposure of the electrode
to the hydrogen. Except for the one value at 4060 ppm of hydrogen, there
is a steady decrease in linearity at higher concentrations of hydrogen.
Actually, in the range of concentrations used, there should be a direct
linear relation of current to concentration, as with the oxygen electrode.
There is, however, a possibility of an "edge" effect with the particular
electrode design, i.e., the hydrogen in excess may diffuse through the
membrane past the platinum electrode and reduce the silver chloride by a
direct reaction without production of an electric current. However,
high concentrations of hydrogen are not of importance for this purpose.
The values indicate that a current amplification of approximately 100
would be required to ensure adequate sensitivity to pentaborane at con-
centrations below 1 ppm, using a galvanometer-type microammeter. This
figure is based on the conversion of the above data from mg/1000 gm to
millimoles of pentaborane per 1000 moles of air, the assumption that roughly
12 molecules of hydrogen are released for every molecule of pentaborane
hydrolyzed, and that the size of the microammeter scale would be 1/10 the
size of the chart recorder currently used to measure the current.

The pentaborane-monitor, platinum-gauze electrode was also tested for sensitivity. Results are presented in Table 4.

TABLE 4

SENSITIVITY OF AN EXPOSED ELECTRODE TO HYDROGEN GAS*

Hydrogen Concentration, mg/1000 gm N_2	Response, microamps	Microamps/ x 10^3 ppm H_2
400	10.8	27.0
1740	36.0	20.7
4000	52.5	13.1
7490	87.4	11.6

*This electrode is about four times more sensitive than the membrane electrode.

Several membranes were also tested for permeability to hydrogen. Nitrogen containing 1740 ppm (w/w) hydrogen was used for the tests. Table 5 indicates that Teflon is the most suitable membrane tested thus far.

The rapid and quantitative conversion of pentaborane to hydrogen is now being tried by passage through a solid support column. As a first attempt, porous, ground fire brick was impregnated with a mixture of ethoxy-ethanol water and sulfuric acid. A stream of helium containing 0.5-percent pentaborane was passed through this column and into a gas bubbler containing a mixture of pyridine and toluene. All of the pentaborane was held in the column as indicated by the absence of a yellow coloration in the toluene solution. However, when the effluent was analyzed for hydrogen using the membrane electrode, it was apparent that the reaction was not rapid, because hydrogen continued to be evolved as long as five minutes after the pentaborane stream was discontinued.

TABLE 5

COMPARATIVE PERMEABILITIES OF VARIOUS FILMS TO HYDROGEN

Membrane	Thickness, mils	Response, microamps
Teflon	1.0	9.5
Teflon (FEP)	0.5	4.5
Polyethylene	1.0	1.5
Cellophane	1.0	0.3
Polyethylene	0.5	4.0

The use of a mild oxidizing agent such as iodine or a silver salt mixed with the solvent is presently being investigated. It has been determined that pentaborane reacts with methyl alcohol much more rapidly in the presence of iodine to form hydriodic acid, hydrogen, and methyl borate.

FUTURE PLANS

The rapid and quantitative conversion of pentaborane is required for the success of the proposed pentaborane sensing devices. Various hydrolytic reagents (e.g., polyglycol and high molecular-weight alcohols) will be impregnated on solid supports (e.g., silica gel, firebrick, etc.) to accomplish this purpose and, if necessary, mild oxidizing agents such as iodine or silver salts will also be included. Previous work on the quantitative determination of pentaborane by titration with a methanol solution of iodine indicates a relatively simple solution to the problem.

Simultaneously with these experiments, work will begin on the use of the membrane electrode to detect oxygen diflouride, hydrazine, nitrogen trifluoride, and chlorine trifluoride in air.

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TASK 3

ANALYSIS OF CRYOGENIC PROPELLANTS

I. Lysyj, Principal Investigator
P. Newton
B. Neale
G. Brull

INTRODUCTION

Task 3 of this program deals with the analysis of cryogenic materials and is directed toward establishing dependable means of analysis for cryogenic hydrogen and fluorine and determination of particulate matter in cryogenic liquids. The first progress report (R-3986), dealing with this project and covering a 6-month period, was issued on 25 January 1963. This presentation covers the 3-month period from 25 December 1962 to 25 March 1963. The material presented in this report is a continuation of work previously reported. References should be made to Rocketdyne report R-3986.

Task 3 is divided into three areas of investigation. Each area is treated separately in this report.

SUMMARY

During the reporting period, a reliability and performance study was con-
ducted using a hydrogen analyzer in conjunction with a Cosmodyne CS-4.4
cryogenic sampler. The study was directed mainly to establishing the
source and magnitude of blank values for hydrogen contaminants. It was
found that the instrument does not produce detectable ($<$ 1 ppm) blanks.
However, the blank of the sampling device, as measured by the oxygen
content, was approximately 80 to 100 ppm.

A mixture of Ne and He was separated on a 20-foot long molecular sieve
5A column held at approximately -78 C, using hydrogen gas as the carrier.

In the study dealing with cryogenic fluorine, characterization and optimi-
zation of the monophase gel column was attempted. It was found that per-
formance of such a column depends in a large measure on the degree of
passivation (or fluorination) of the column. The best conditions for the
separation of impurities reported in fluorine (SiF_4, CF_4, NF_3, SF_6) were
established using columns 24 and 34 feet long. The Cosmodyne cryogenic
fluorine sampling device was received and will be tested.

The quantitative approach for the determination of particulate matter
in liquids using the device described in the previous report was attempted
using Al_2O_3 powder (granular) and Al (flakes) suspended in water. The
results indicate some qualitative relationships but additional work must
be done before any quantitative conclusions can be drawn or any design
parameters called out for cryogenic systems.

Diagrams of the hydrogen analyzer and fluorine gas chromatograph, plus
the literature search on related subjects will be presented in the final
report.

ANALYSIS OF CRYOGENIC HYDROGEN

The data dealing with the determination of ortho-para hydrogen ratios were presented in the last report. The present report considers the reliability and performance of the hydrogen analyzer in the determination of trace impurities at the 1-ppm level. To evaluate the performance of the instrument and technique at such extremely low concentration levels, care must be taken to minimize the contribution of blank values. The blank values at these levels might contribute considerably to the results, changing them by an order of magnitude or greater. To illustrate the point, a research grade of hydrogen gas (the purest grade available in large quantities) made by the Matheson Co., might contain as much as 10 ppm O_2, 1500 ppm N_2, and 100 ppm CO_2 (Ref. 8). It is obvious that even using the best grade of hydrogen gas as a carrier without prepurification, the detection of 1 ppm of O_2 or 10 ppm of N_2 in a gas sample is meaningless. It is also obvious that contamination of the sample by atmospheric gases during the sampling procedure or in the instrument can easily change the result by several orders of magnitude.

Realizing the difficulty of analyzing for atmospheric gases in the ppm range, a concentrated effort was directed toward the evaluation of the capabilities of the hydrogen analyzer for the analysis of impurities at that level. The blank can obscure the analysis at two points by: (1) contamination of the sample during the sampling procedure, (2) contamination of the sample during the analysis. This problem was thoroughly investigated during the reporting period. The linearity of response and the trapping efficiency of the purification and collection traps were also investigated to provide a complete understanding of the instrument's function.

PROCEDURE

The instrument was operated essentially as described in the previous report. Because of the danger of the carrier gas contributing to the blank

values, column C_1 (purification) was lengthened to 6 feet and packed with activated charcoal. The instrument operated under the following conditions:

Flowrate	110 cc/min
Carrier	H_2 (purified in C_1)
Detector voltage	8.6 volts
Detector temperature	28 C
Analyzer column	5-foot Linde sieve 5A, 3/16-inch tubing
Column temperature	25 C
Recorder	L & N Speedomax, 10 mv

Evaluation of Blank Contribution by Instrument

The critical area for leaks in the instrument (Fig. 1) is between traps C_1 and C_2. Any leak contribution before C_1 will be eliminated by the purification trap. The sample passes from C_2 directly to the detector. If a leak occurs in this section it will be detected easily by an increased instrument response. The following experiment was conducted to check the blank contribution of the instrument. An LN_2 trap was placed on the C_1 column, purifying the hydrogen gas stream. A second LN_2 trap was placed on the C_2 column to collect any contaminants introduced by leakage between the C_1 trap and the detector. The collection was conducted over various periods of time and, in all cases when the instrument was operating properly, no blank was observed. The instrument was shut off and leak tested whenever blanks were observed while using this procedure. Operations were resumed after the leaks were eliminated.

Evaluation of Blank Contribution
by the Sampling Device

While the Cosmodyne cryogenic liquid sampler, Model No. CS-4.4, is described in detail in the Cosmodyne instruction manual, a brief description may prove helpful. The sampler consists of a 4.4-liter metal outside container
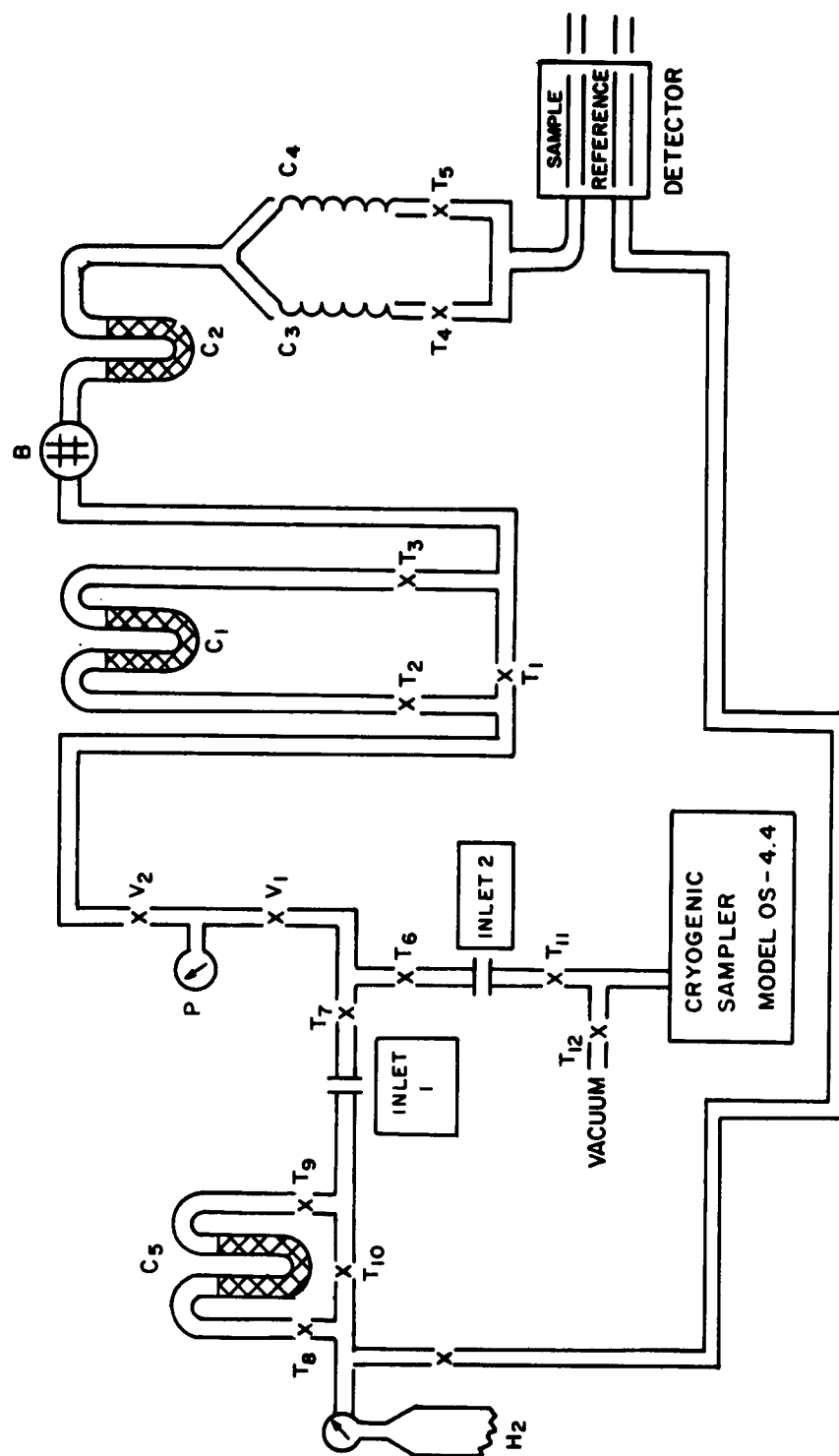
Figure 1. Hydrogen Analyzer Flow System

which is evacuated to less than a 100-micron pressure prior to use. A line, through which the cryogenic liquid flows, passes through the center of the sampler. The cryogenic liquid is allowed to pass through this line to cool the apparatus. A sample cup directly connected to the outside metal container is situated within this cryogenic liquid stream. When the entire line is cold, as evidenced by a constant stream of liquid from the exit of the container, a valve between the gas stream and the sample cup is opened. A quantity of liquid is sucked up into the cold cup and the valve is closed. The liquid stream is then discontinued, and the sampler is allowed to warm up. The final pressure at room temperature is about 400 psi. The sampler is connected to whatever apparatus is desired through a valve at the bottom of the sampler.

Since there is no way to obtain a standard sample of liquid hydrogen, it was decided to load a previously calibrated sample directly from a K bottle into the sample container. The purpose was to simulate sample conditions as much as possible. The gas sample from a K bottle was analyzed using the hydrogen analyzer prior to sampling with the Cosmodyne cryogenic sampler. The established procedure is described in the following paragraph. Column parameters are as described under the Procedure Section.

The K bottle of hydrogen is hooked to the line which runs through the sampler (evacuated to a 50-micron pressure). Tests indicated there is no air leakage. A valve is connected to the exit line. H_2 from the K bottle is allowed to flow through at a high flowrate. After 200 psi are removed from the K bottle, about 10 minutes, the valve on the outlet is closed. The pressure is then increased to 300 psi (the limit of the regulator), and the valve controlling the sample cup is opened. The container immediately fills to 300 psi. The valve is closed, and the system is depressurized and disconnected. The sampler is then ready to run as a normal sampler that has been normally charged.

The samples of H_2 from the K bottle were contaminated during the transfer to the cryogenic sampler as Table 6 indicates, and certain modifications of the cryogenic sampler, Model No. CS-4.4 will be necessary if it is to be used for analysis of ppm contamination in liquid hydrogen.

TABLE 6

ANALYSIS OF HYDROGEN GAS FROM K BOTTLE AND

AFTER TRANSFER TO THE CRYOGENIC SAMPLER CS-4.4

Sample	Duplicate Direct Analysis of H_2 From K Bottle, ppm (v/v)		After Transfer to Sampler, ppm (v/v)
N_2	131	140	280
O_2	3.1	3.8	80

Linearity of Response

The linearity of the response was checked out using standard loops in the Beckman valve. Inspection of Fig. 2 shows that the linearity of response for both O_2 and N_2 is satisfactory. The interscale linearity is perfect. One cc on the X14 scale produced responses of 0.7 mv and 2.0 mv for O_2 and N_2, respectively. On the X54 scale, the responses were 2.7 mv and 7.7 mv, which was predicted.

Trapping Efficiency

There is a possibility that during operation the impurities are not retained in the trapping columns. The efficiency of C_1 was proved by trapping impurities on both C_1 and C_2. No material was obtained in C_2 during runs for periods as long as 60 minutes. The efficiency of C_2 was proved by injecting 1.0 cc of air directly into C_2 under trapping conditions, while hydrogen flowed continuously.

Inspection of Fig. 3 shows that, within experimental error, for up to 1/2 hour no material is removed from C_2. Figure 4 shows the effect of continuous trapping of impurities in C_2 from a sample of gaseous H_2. If the material eluted from C_2 as C_2 became saturated, the curves would tend to fall off at longer periods of time. As can be seen, the lines are perfectly straight. One additional fact should be emphasized at this
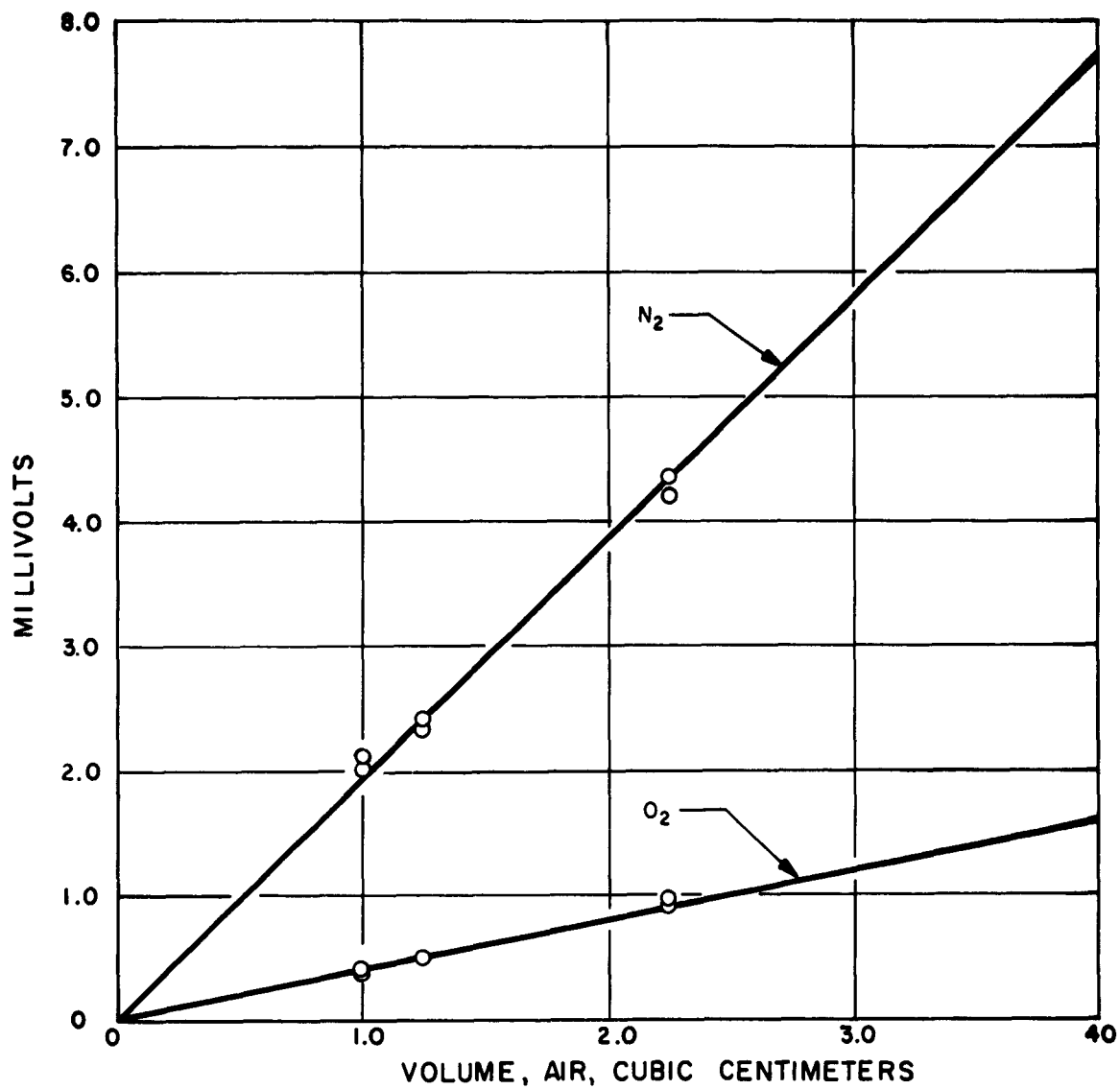
Figure 2. Linearity of Response: The Effect of Known
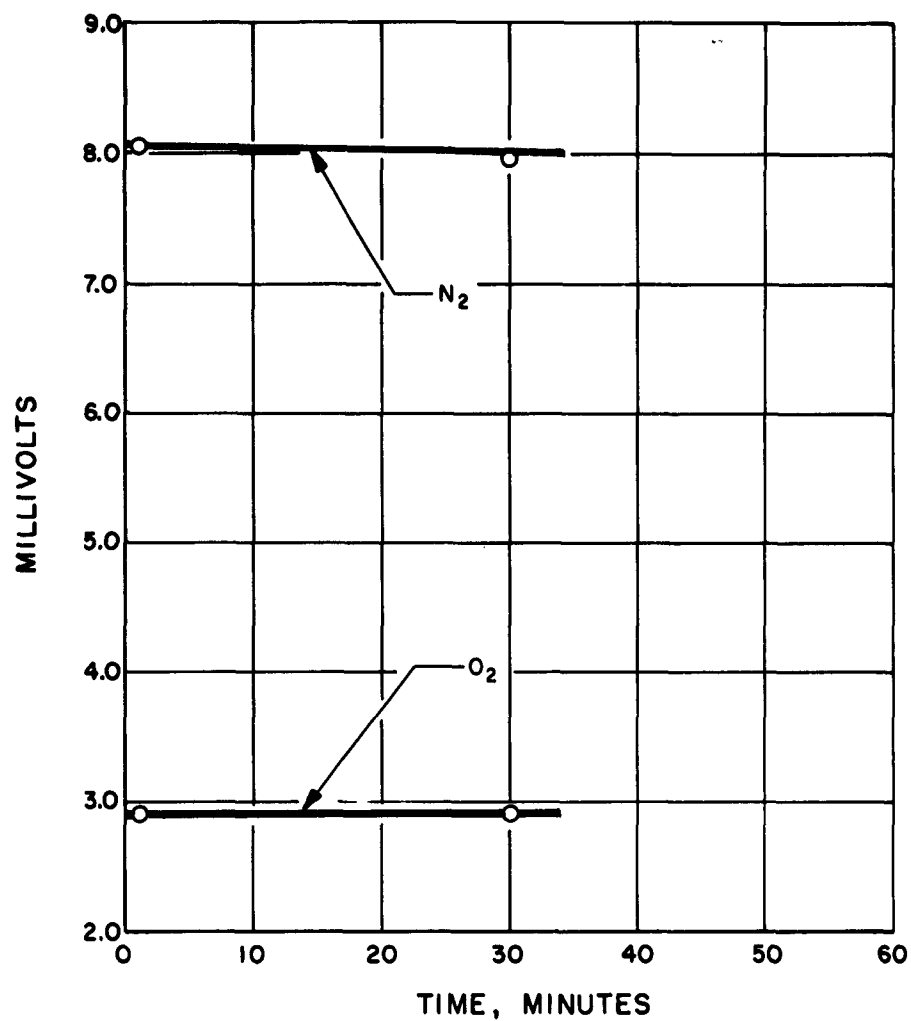Quantities of Air on the Instrument

Figure 3. Trapping Efficiency: The Effect of Passing
Pure Hydrogen Through a Trap, Using a Known
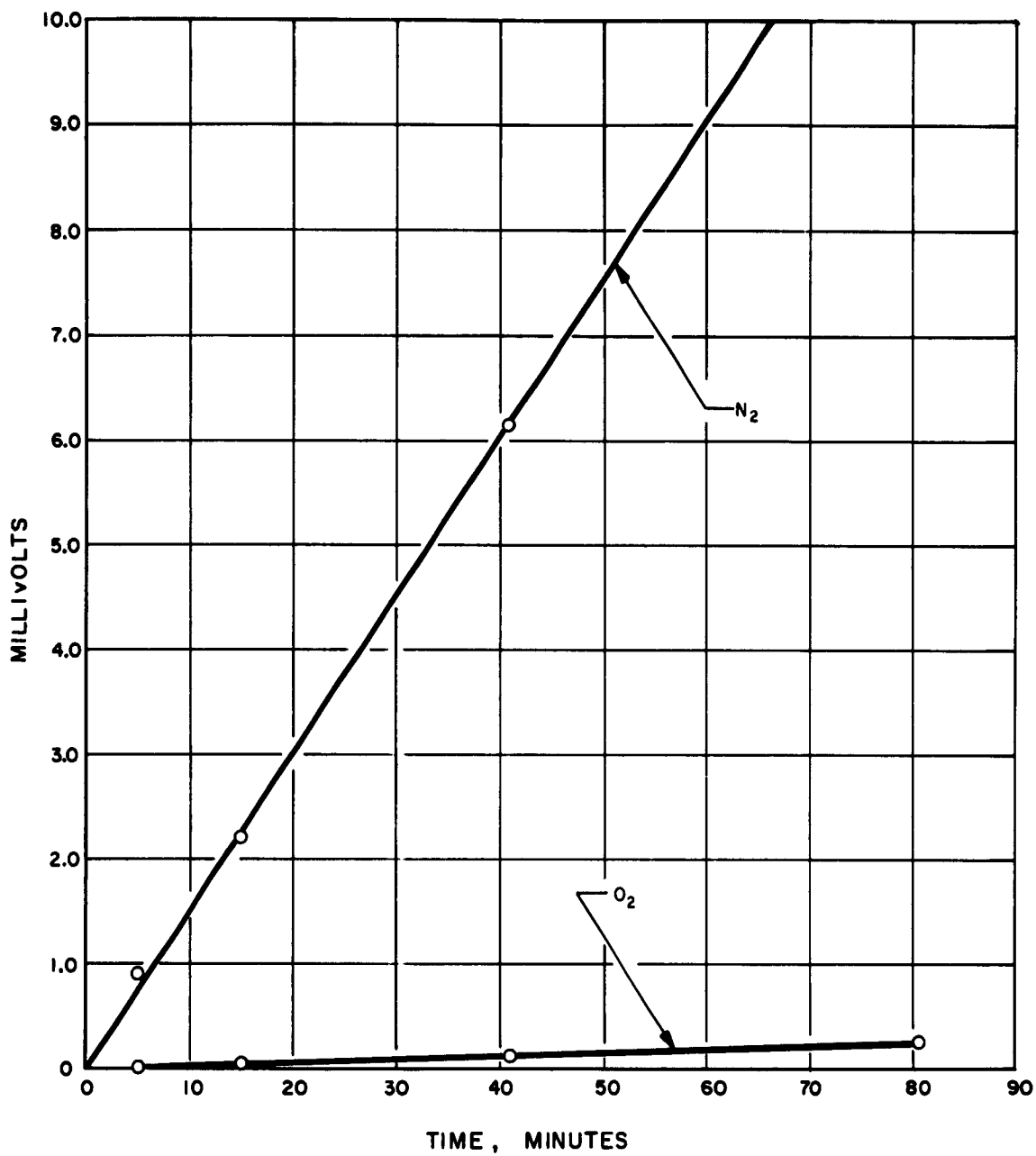Amount of Air

Figure 4. Trapping Efficiency: The Effect of
Trapping Impurities for a Long Length
of Time

point. No peaks were observed when a relatively large amount of air (1 cc at STP) was introduced in C_2. This indicates that trapping is excellent.

Although the detector and the column are between C_2 and the atmosphere, the low pressure produced when C_2 is suddenly cooled from 300 to 80 K could suck air back into C_2. It has not been shown definitely that this occurs. It is recommended, however, that T_4 be closed whenever LN_2 is added to either C_1 or C_2, or that an activated charcoal trap immersed in LN_2 be placed at the exit of the instrument. This also aids in obtaining a stable baseline more quickly. In addition to a pressure drop when LN_2 is put on C_2, there is a pressure rise when the LN_2 is removed. To keep the material in C_2 from being blown back to C_1, a check valve was introduced in the line between them. It appears that the apparatus is working satisfactorily at the levels of impurities encountered in current H_2 samples.

Separation of He and Ne in a Hydrogen Gas Matrix

Since He and Ne might be present in a sample of cryogenic hydrogen, determination of these materials is desirable in some cases.

Several experiments were conducted using various columns, conditions, and carrier gases to provide satisfactory gas chromatographic separation of these elements. A satisfactory procedure was developed and optimized for such a separation.

Apparatus. A conventional Perkin-Elmer 154D gas chromatograph was used in this study. The column coil was connected to a detector cell by two U-tubes. The column was filled with molecular sieve 5A and located externally to permit placement of a cold layer over it.

The optimum conditions for separation of He and Ne are:

1. Instrument   Perkin-Elmer 154D with 8000-ohm thermistor detection

2. Carrier gas   Hydrogen, inlet pressure = 29 psig, flow = 7 cc/min

3. Sample   Mixture of He and Ne, 1 cc injected by means of Perkin-Elmer gas sampling valve

4. Column   20 feet long, 1/4-inch diameter, packed with molecular sieve 5A, 50 to 80 mesh size, column kept outside the instrument

5. Temperature   Detector, approximately 25 C Column, approximately -78 C

6. Sensitivity   128

7. Detector Potential   9.0 volts

8. Recorder   Leeds & Northrup Model-H, 1 mv full scale, speed = 1/2 inch per minute

Results. A prepared mixture of He and Ne was analyzed mass spectrometrically, and then by gas chromatography. The results of this analysis are presented in Table 7. The chromatograms of He and Ne separation at ambient temperature and -78 C are presented in Fig. 5. The correction factors are based on mass spectrometric analysis.

CONCLUSION AND FUTURE WORK

The hydrogen analyzer was extensively tested and found to be satisfactory for the determination of ortho-para hydrogen isomers and the following impurities in the ppm range: N_2, O_2, CO, and CH_4. The cryogenic sampling device, Model No. CS-4.4, made by Cosmodyne, was found to be unsatisfactory for trace determination of impurities in cryogenic hydrogen below the 100-ppm level. This is probably due to the small degree of leakage and can

Gas Chromatograph of He-Ne Mixture

Conditions

Carrier Gas:	H_2, inlet pressure-29 psig, flow-7 cc/min
Column:	20 feet x 1/4-inch diameter, molecular sieve 5A - 50 to 80 mesh size
Temperature:	Approximately 25 C
Bridge Potential:	9.0 volts
Sensitivity:	128
Recorder:	Leeds and Northrup Model H, 1 millivolt full scale, speed 1/2 inch per minute
Instrument:	Perkin-Elmer 154D

Gas Chromatograph of He-Ne Mixture

Conditions

Carrier Gas:	H_2, inlet pressure-29 psig, flow-7 cc/min
Column:	20 feet x 1/4-inch diameter, molecular sieve 5A - 50 to 80 mesh size
Temperature:	Approximately -78 C
Bridge Potential:	9.0 volts
Sensitivity:	128
Recorder:	Leeds and Northrup Model-H, 1 millivolt full scale, speed 1/2 inch per minute
Instrument:	Perkin-Elmer 154D

Gas Chromatograph of He-Ne Mixture

Conditions

Carrier Gas: H₂, inlet pressure-29 psig, flow-7 cc/min
Column: 20 feet x 1/4-inch diameter, molecular
                 sieve 5A - 50 to 80 mesh size
Temperature: Approximately 25 C
Bridge Potential: 9.0 volts
Sensitivity: 128
Recorder: Leeds and Northrup Model H, 1 millivolt
                 full scale, speed 1/2 inch per minute
Instrument: Perkin-Elmer 154D

He

Gas Chromatograph of He-Ne Mixture

Conditions

Carrier Gas: H₂, inlet pressure-29 psig, flow-7 cc/min
Column: 20 feet x 1/4-inch diameter, molecular
                 sieve 5A - 50 to 80 mesh size
Temperature: Approximately -78 C
Bridge Potential: 9.0 volts
Sensitivity: 128
Recorder: Leeds and Northrup Model-H, 1 millivolt
                 full scale, speed 1/2 inch per minute
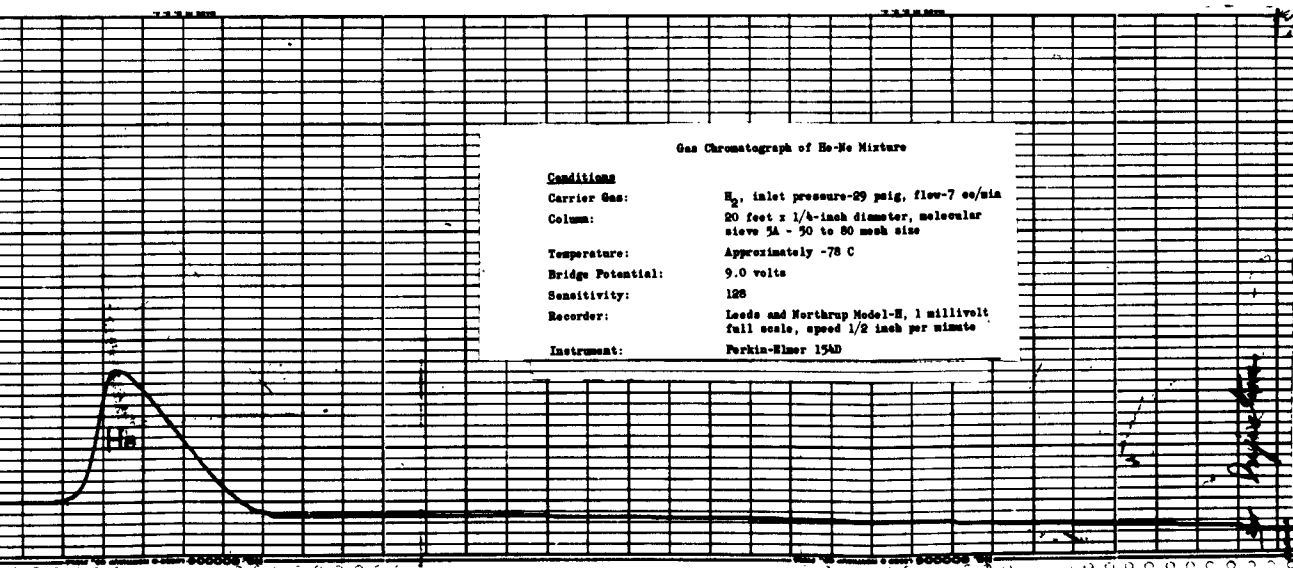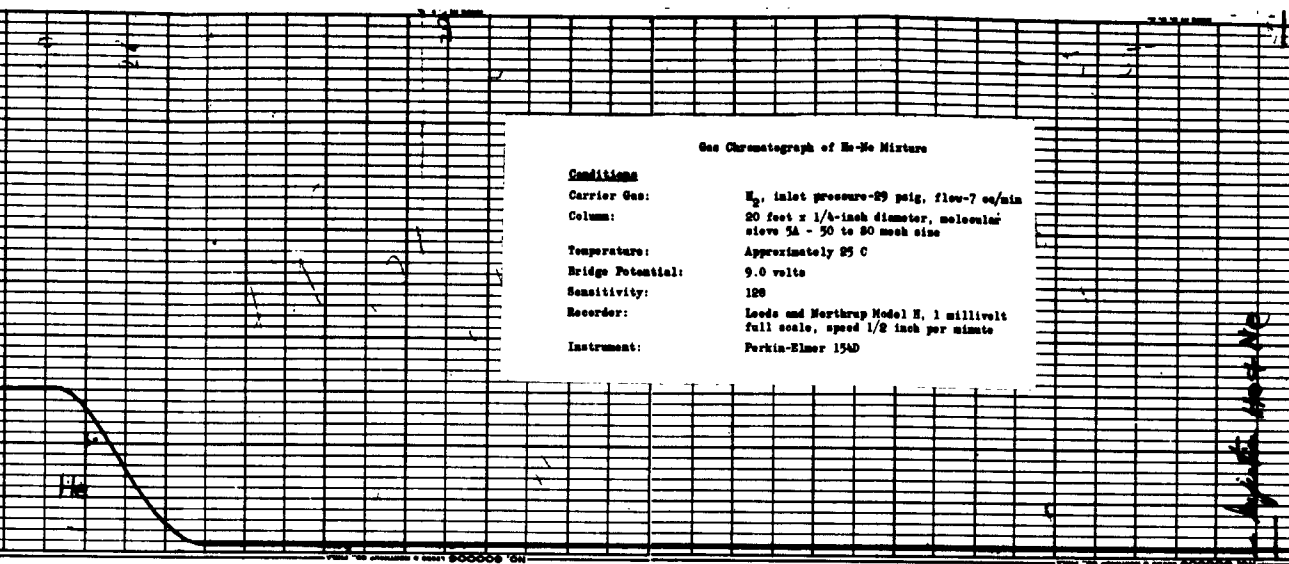Instrument: Perkin-Elmer 154D

He

Figure 5. Chromatograms of
He and Ne Separation

be corrected by certain modifications of the sampling device. However, the sampling device is satisfactory for analysis of the ortho-para isomer ratio in hydrogen.

TABLE 7

SEPARATION OF HE-NE MIXTURE*

	He	Ne
Composition (mass spectrometrically), percent	70.5	28.9
Integrated Areas by Planimeter (gas chromatography), sq in.	1.88	2.94
Correction Factors for Instrument Response (calibration)	X37.45	X9.73
Thermal Conductivity, $\lambda \times 10^5$ at 0 C	33.60	10.87
Retention Time (peak maxima), minutes	28.0	34.5
Retention Volume, cc	196	241.5
Number of Theoretical Plates Per Foot of Column	39.2	46.3

*Sample also contained 0.6 percent of air

The instrumentation system described is simple and easy to operate, and provides a method for analysis of possible atmospheric contaminants such as nitrogen and oxygen, and contaminants due to the manufacturing process, such as methane and carbon monoxide. These are the most critical contaminants in cryogenic hydrogen since they remain in the solid state at the temperature of liquid hydrogen. The separation of He and Ne was accomplished, and the analytical procedure for their determination at higher concentration levels is described. For the determination of these materials at trace levels (ppm), a more sensitive detection system than those presently available commercially is necessary.

The hydrogen impurities preconcentrator made by Cosmodyne will be tested.

ANALYSIS OF CRYOGENIC FLUORINE

To the present time only a monophase gel column has been found satisfactory for the gas chromatographic analysis of fluorine. For this reason, a broad analytical study dealing with the performance of the monophase gel column was conducted over the reporting period. The study was oriented toward a basic understanding of fluorine behavior in the instrument, column, and detection system. Long columns (24 and 34 feet) were studied to provide better separation between fluorine contaminants. No attempt has been made to establish the analytical procedure at this time, because more basic information is considered necessary before the attempt. Additional instrumental approaches to the analysis of fluorine and its contaminants should be undertaken. The capillary columns with electron capture detection might provide a more sophisticated and advanced means of analysis for this highly reactive material.

APPARATUS

The gas chromatographic column used in this study was prepared from three 8-foot sections of stainless-steel tubing (1/4-inch OD), although monel or nickel tubing will be used in the final design. After filling, the columns were individually coiled into spirals approximately 5 inches in diameter and connected by means of AN fittings. The substrate was held in the column by means of a few circular sections of porous Teflon inserted in a short piece of Teflon tubing of suitable diameter to allow a snug fit in the ends of the stainless-steel tubing. The fluorine analyzer used (Fig. 6 and 7) was described in the previous report for this program.

To provide for greater resolution between fluorine contaminants, an attempt was made to prepare and characterize a longer gel column.
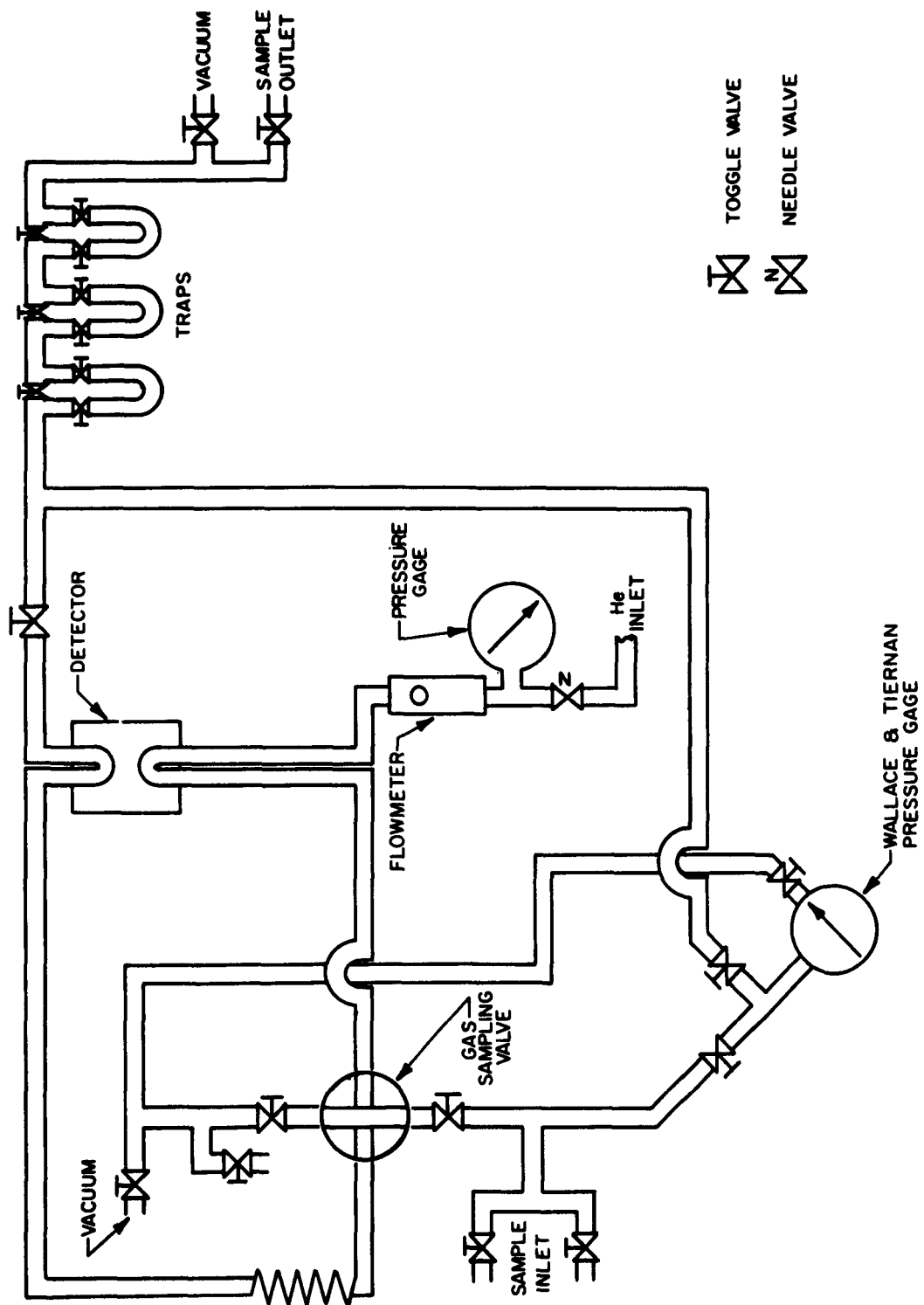
Figure 6. Gas Chromatograph for Fluorine Analysis
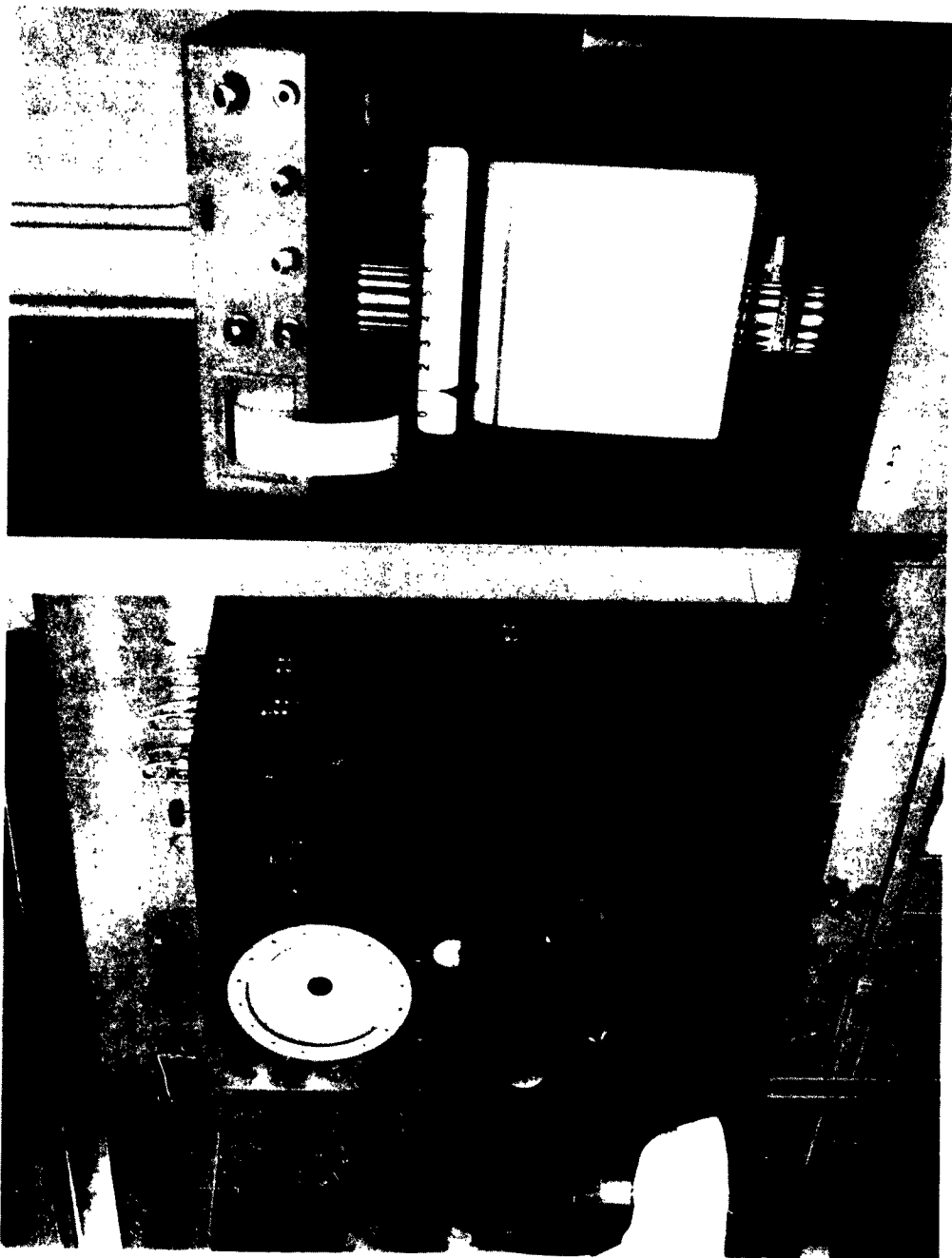
TOGGLE VALVE

NEEDLE VALVE

VACUUM

SAMPLE OUTLET

TRAPS

DETECTOR

PRESSURE GAGE

FLOWMETER

He INLET

WALLACE & TIERNAN PRESSURE GAGE

GAS SAMPLING VALVE

VACUUM

SAMPLE INLET

Figure 7.　Fluorine Analyzer

6AD42–2/14/63–C1B

The column packing was made from Halocarbon Oil 13-21 and Kel-F molding powder 300, 30 to 50 mesh, in the manner described in the previous report, and packed in a conventional manner. The resulting filled column contained approximately 5 grams of material per foot. The passivation of the column and the instrument was attempted by introducing successive samples of ClF_3.

EXPERIMENTAL

The column was characterized by analysis of SiF_4 at varying flowrates. A height equivalent theoretical plate (HETP) vs flowrate curve was established. The data and curve are presented in Table 8 and Fig. 8 , respectively. The optimum gas flow for this 24-foot column was found to be in the 35 to 45 cc/min region.

To increase further the resolution of the column, an additional 10-foot length of gel column, which had been used previously for highly reactive materials, was added giving a total of 34 feet of gel column. This combined column was also characterized using SiF_4 as the test material. The results and the HETP vs flowrate curve are found in Table 9 and Fig. 9 , respectively. The optimum gas flows were found to be in the 40 to 50 cc/min region.

In another series of experiments a comparison of the performance of the older 10-foot section of column and the newer 24-foot section of column was made using Freon-12 as the test sample. A comparison of the retention times indicated that the older 10-foot section was about equal in retentive power to the longer 24-foot section of column. This indicated that the newer 24-foot column required additional treatment. To accomplish this, the column was removed from the instrument, one end capped tightly, and evacuated, after which an atmosphere of fluorine was introduced. The column was allowed to remain closed off overnight. During this period the fluorine pressure had decreased appreciably, indicating that the fluorine had been used up by the column packing or the material of construction. The procedure was repeated, this time for 3 hours. The column was then flushed out with helium and replaced on the instrument.

TABLE 8

CHARACTERIZATION OF 24-FOOT GEL COLUMN

F[*]	R_t[**]	R_v[***]	N[****]	HETP Centimeters
7.8	18.0	140	24	1.172
15.6	11.7	183	27	1.055
20.8	8.5	177	30	0.932
31.2	6.0	187	39	0.726
42.0	4.4	185	44	0.640
56.0	3.6	202	38	0.807
115.0	1.8	207	25	1.115

Carrier Gas — — Helium	Sample — SiF_4
Column Pressure — 20 psi	Bridge Current — 200 ma

[*]F   = Flow, cc/min

[**]R_t = Retention time

[***]R_v = Retention volume
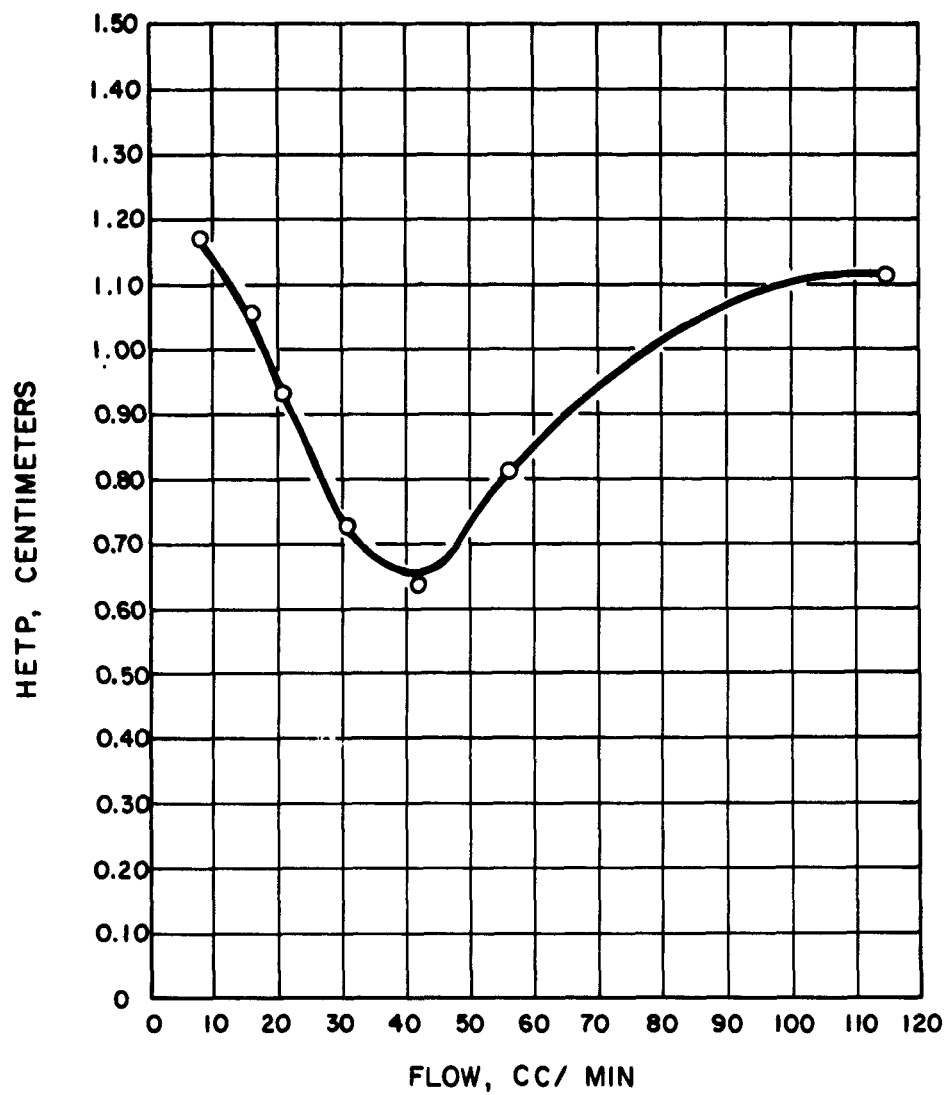
[****]N   = Number of theoretical plates per foot of column

Figure 8. HETP vs Flowrate Curve for 24-foot Gel Column

36

TABLE 9

CHARACTERIZATION OF 34-FOOT GEL COLUMN

F*	R_t**	R_v***	N****	HETP Centimeters
4	33.7	135	37	0.824
8	25.4	203	45	0.679
16	15.9	254	61	0.502
23	10.7	246	54	0.566
32	7.8	250	58	0.522
43	5.8	244	63	0.481
72	3.5	252	36	0.846
84	2.8	235	23	1.325

Carrier Gas — Helium	Sample — SiF_4
Column Pressure — 20 psi	Bridge Current — 200 ma

$*F$ = Flow, cc/min

$**R_t$ = Retention time

$***R_v$ = Retention volume

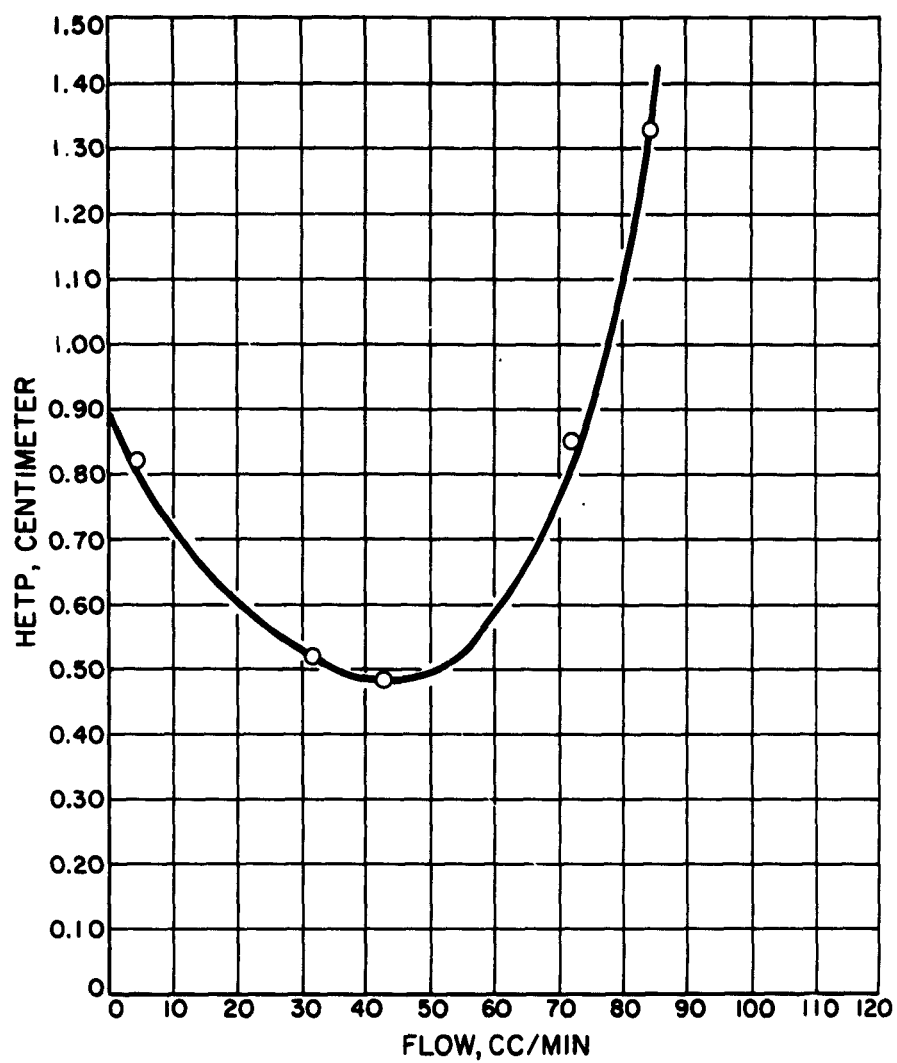$****N$ = Number of theoretical plates per foot of column

Figure 9. HETP vs Flowrate Curve for
34-foot Gel Column

Runs of fluorine samples were made and the response indicated that the
24-foot column was still consuming most of the fluorine. Successive runs
of SiF_4 gave little or no response, indicating the presence of moisture
on the column. The column was again removed from the instrument and a
total of about 10 cc of liquid ClF_3 was allowed to expand through the
column over a period of about 4 hours. This drastic treatment apparently
removed the moisture because, on ensuing runs of SiF_4, the response
approached that of air. The ClF_3 treatment also apparently rendered the
column more retentive based on a longer retention time for ClF_3.

Additional comparisons were then made with the 24-foot column and the
combined 24- and 10-foot (34 feet) column. SiF_4, CF_4, SF_6, F_2, NF_3, Cl_2,
ClF_3, Freon-12 and Freon-13 were run and the number of theoretical plates
per foot of column, retention time, and retention volumes are reported
in Table 10 and 11. The data in these tables indicate that, although the
shorter 24-foot column gave a greater number of theoretical plates per
foot than the 34-foot column, the longer column rendered greater separation.

DISCUSSION

While a column capable of analysis of such a highly reactive material as
fluorine is available, a number of questions concerning associated problems
and techniques of analysis remain unanswered. The monophase gel column
prepared by plasticizing Kel-F molding powder with large amounts of halo-
carbon oil has unique properties. The retention volumes for fluorinated
materials obtained with this column were dramatically higher than retention
volumes obtained on duophase-type column packing. This can be explained
in part by a modified equation dealing with absolute retention volume:

$$V_R = V_A + \left(1 + \frac{K \cdot V_L}{V_m}\right)$$

where:

V_R = Retention volume (adjusted to column temperature)

TABLE 10

PERFORMANCE OF 34-FOOT GEL COLUMN

Material	R_t^*	R_v^{**}	N^{***}
Air	6.0	258	35
CF_4	6.3	271	15
SiF_4	6.8	292	10
NF_3	6.8	292	10
SF_6	8.8	378	4
F_2	18.3	787	2
Cl_2	26.2	1127	4
ClF_3	27.8	1195	1
Freon-12	26.5	1140	1
Freon-13	9.2	396	3

Column Pressure – 20 psi	Carrier Gas – Helium
Flowrate – 43 cc/min	Bridge Current – 200 ma

$*R_t$ = Retention time

$**R_v$ = Retention volume

$***N$ = Number of theoretical plates per foot.

TABLE 11

PERFORMANCE OF 24-FOOT GEL COLUMN

Material	R_t*	R_v**	N***
Air	4.5	194	54
CF_4	4.8	206	62
SiF_4	4.7	202	41
NF_3	5.1	219	21
SF_6	6.2	267	6
Cl_2	21.7	933	5
ClF_3	21.7	933	4

Column Pressure	− 20 psi	Carrier Gas	− Helium
Flowrate	− 43 cc/min	Bridge Current	− 200 ma

*R_t = Retention time

**R_v = Retention volume

***N = Number of theoretical plates per foot

V_A = Retention volume of unabsorbed solute (adjusted to column temperature)

V_L = Volume of liquid phase in column (at the column temperature)

V_m = Volume of mobile gas phase in column equal to free space in the column

K = Partition coefficient

This equation indicates that, with an increase of liquid phase in the column, retention volumes do increase. Since the gel column used in this work contains a 50-percent liquid phase, longer retention times must be expected. The other reason for the considerable increase of retention times for fluorinated materials may be found in the extreme selectivity of this type of column to the fluorinated compounds. Our experience with the use of a monophase gel column indicates that the substrate behaves dynamically and with prolonged use of the Kel-F-halocarbon substrate for the analysis of reactive fluorine compounds performance of the column improves.

The reason for such behavior is unknown at the present time. It is believed that physical and/or chemical changes, such as an additional fluorination of the substrate, do occur on the column. The study of this phenomenon is made difficult by the reaction between fluorine and metals used in the physical design of instrumentation. While stainless-steel materials can be passivated and made essentially inert to the fluorine, they depassivate with ease. This introduces additional unknown parameters in any attempt to find a rational basis for the behavior of reactive fluorine-containing materials on the Kel-F-halocarbon oil column.

CONCLUSIONS AND FUTURE WORK

The results of this study indicate that a monophase gel column (Kel-F-halocarbon oil) of suitable length, conditioned by ClF_3, can be used for gas chromatographic analysis of fluorine and its contaminants. However, a more sensitive detection system than the Teflon-coated hot-wire filament is necessary for analysis of trace contaminants in fluorine. The

study also indicates that each newly made column must be optimized and characterized with respect to the separation of materials of interest, because no direct comparison exists between columns prepared and conditioned on different occasions.

An evaluation of a Cosmodyne cryogenic sampling device for liquid fluorine is planned for the next quarter. An attempt to prepare a semimicro (1/8-inch diameter) gel column 30 to 50 feet in length is planned. Such a column might provide a higher degree of resolution for materials of interest and, when used in conjunction with an electron capture detector, might provide a satisfactory system for analysis of cryogenic fluorine for contaminants.

C

TASK 4

ANALYSIS OF PENTABORANE-HYDRAZINE FIRING RESIDUES

R. C. Greenough, Principal Investigator

D. V. Owens

CRYOGENIC PARTICULATE MATTER DETECTOR

Additional experiments are being carried out on the problem of detecting
particulate matter in cryogenic fluids. The preceding progress report
described the design and construction of a detection device based on the
measurement of pressure drop across a filter. The results obtained indi-
cated, at least qualitatively, several relationships between the various
operating parameters. If quantitized more thoroughly, these relation-
ships might permit setting up a combination detection and "scavenging"
device applicable to cryogenic storage monitoring. The work performed
during this report period was devoted to evaluating the effect of differ-
ent particle shapes and materials and an attempt to obtain more quantita-
tive results. Unfortunately, results so far obtained are still inconclu-
sive and not amenable to quantitative interpretation. For this reason
discussion of this effort will be postponed until the final report.

SUMMARY

The composition of the samples of firing residues under investigation
has now been explained. Borazole and, subsequently, polyborazole have
been synthesized, and the latter has been subjected to elemental analysis.
Differential thermal analysis shows that the only reaction of polyborazole
is the endothermic evolution of hydrogen. Mass spectrometric evidence in-
dicates that the hydrogen is released monatomically.

EXPERIMENTAL

FIRING RESIDUES

In the previous report, the elemental analysis of a firing residue was given. The presence of large amounts of oxygen as well as a small amount of carbon in the solid, and a small amount of HCN in the gas was unexplained, until it was learned that the hydrazine line had a water leader and the pentaborane line had a toluene leader. This explained the source of the extraneous materials.

The amount of hydrogen gas in the sampling device was calculated from the gas law to be 0.79 mole. From the 1.87 grams of solid sample removed from the sampler, assuming that it was pure BN, only 0.16 mole of hydrogen could be generated. This factor-of-5 discrepancy indicated that the solid that should have been associated with the gas either was not collected through the sampling orifice in the chamber wall or was held in the line connecting the chamber with the sampler. The latter was evidently the case, as solid was found in the line on disassembly.

From the elemental analysis on a dry basis, the following number of moles was calculated to be in the 1.87 grams of residue:

$$B \;=\; 0.0766 \text{ mole}$$

$$N \;=\; 0.0496 \text{ mole}$$

$$O \;=\; 0.0168 \text{ mole}$$

It is interesting to note that the oxygen present in the solid, both as H_2O and combined oxygen, required only 300 mg of water to be present initially. All these elements can be theoretically distributed into three compounds, B_2O_3, BN, and B. This is not necessarily the way the elements are distributed in the solid. Indications are that the solid is a very complex mixture of compounds of an unknown nature.
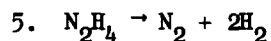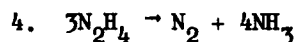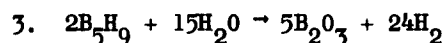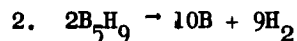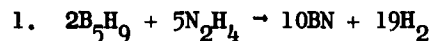
The results of such a distribution are:

$$BN = 0.0496 \text{ mole}$$

$$B_2O_3 = 0.0056 \text{ mole}$$

$$B = 0.0158 \text{ mole}$$

The propellants and water may react in the following ways to produce hydrogen or other gaseous products, and the solids as given just above:

1. $2B_5H_9 + 5N_2H_4 \rightarrow 10BN + 19H_2$

2. $2B_5H_9 \rightarrow 10B + 9H_2$

3. $2B_5H_9 + 15H_2O \rightarrow 5B_2O_3 + 24H_2$

4. $3N_2H_4 \rightarrow N_2 + 4NH_3$

5. $N_2H_4 \rightarrow N_2 + 2H_2$

The amount of hydrogen released by the pyrolysis of toluene was neglected because the amount of carbon found in the residue corresponds to less than 0.0025 mole of H_2. The amount of hydrogen was calculated for 1.87 grams of solid of the above composition. Using this value to prorate the total amount of gas considered produced at the same time, the amount of N_2 was calculated. This, in turn, permitted the calculation of the hydrogen formed in reaction. The calculation was repeated until a consistent answer was obtained.

There are now values for the amounts of BN in the solid, NH_3 in the solid, N_2 gaseous, and NH_3 gaseous. The total amount of nitrogen was found to be 0.0760 mole, which is almost equal to the 0.0766 mole of boron found. The agreement is striking because the firing ratio of pentaborane and hydrazine was stoichiometric. The agreement implies, therefore, that the oxygen present was added to the solid after combustion had taken place, presumably during the sampling.

POLYBORAZOLES

The products yielded by the pyrolysis of borazole, $B_3N_3H_6$, are called
polyborazoles. Analyses of these materials were carried out by wet
methods, infrared, differential thermal analysis, and mass spectrometry.

Preparation

The borazole was prepared by the reaction of trichloroborazole with
lithium borohydride. A sample of it was pyrolyzed at 485 C for 72 hours.
Yield of recoverable solid was only 500 mg. The material formed was very
hard and, therefore, difficult to chip from the sides of the flask. The
possibility exists of a slight leak in the system which would have per-
mitted some borazole to escape, resulting in an apparent low yield.

Wet Analysis

Wet analysis of the polyborazoles was performed for both boron and nitro-
gen. For the first analysis for boron, the sodium carbonate fusion fol-
lowed by titration of boric acid in mannitol was used. The results
showed only 30 percent boron present. It was suspected that some com-
ponents of the mixture had been volatilized during the fusion. An
investigation was made of the possibility of using the Schöniger oxygen
flask combustion for converting the boron to an analyzable form. It was
unsuccessful because the sample could not be kept in the combustion zone.
It was scattered away from the flame by the heat and did not burn. A
milder method of attack was alkaline hydrolysis, both hot and cold.
The cold-hydrolyzed material appeared to contain 45.8 percent boron.
The latter value is close to the 44 percent boron in pure BN.

Nitrogen was determined by the micro-Kjeldahl method. The polyborazole
was found to contain 44.7 percent nitrogen. This is much lower than
expected. Borazole itself has 51 percent nitrogen, while BN, its

ultimate decomposition product, has 56 percent nitrogen. A check will be made on the determination of nitrogen by the modified Dumas method.

Vacuum Pyrolysis

The induction furnace method was used to determine the total hydrogen content of the polyborazole. Three samples were heated to 1100 F, and the hydrogen given off was oxidized by hot CuO to H_2O which was collected in an ascarite absorption tube. Values of 4.6, 7.0, and 7.1 percent were obtained. The first value is reasonable, but the others are not, because borazole itself contains only 7.5 percent hydrogen. The residue from the third combustion was analyzed and found to contain only 30 percent boron.

Differential Thermal Analysis

The polyborazole was investigated by differential thermal analysis (DTA). The first sample run showed a sharp endothermic drop at 90 C. The DTA curve then remained a constant distance below the baseline to 180 C, at which point there was a sharp return to the baseline. Small endotherms were observed at 202 C and 314 C.

It was suspected that the small endotherms were a result of interaction with the alumina used as the inert diluent and reference. The alumina to be used as the diluent for the sample was heated before another sample was added. The DTA curve of this sample now showed only the sharp endothermic break at 45 C and the equally sharp return to the baseline at 225 C. This sample was cooled and then run through the heating cycle again. This time the baseline was smooth and undisturbed.

Mass Spectrometry

A sample of the polyborazole was placed in a low-temperature Knudsen cell in the time-of-flight mass spectrometer. At first, only water vapor

appeared up to 50 C. The H_2O disappeared, and hydrogen atoms were observed. No hydrogen molecules were found. There was some boron and nitrogen but not in amounts comparable to the hydrogen.

DISCUSSION

The nature of the firing residues examined has been well defined by the
analyses given in this and the previous quarterly report. The most im-
portant point brought out is that the total B/N ratio from all the products
of the firing is almost precisely that of the firing mixture. The oxygen
found in the solid came from water of the water lead that was held up in
the sampling line. The small amount of water necessary to account for all
the effects is not unreasonable. The concentration of water in the hydrazine
is not sufficient to account for the large water to hydrazine ratio.

The small amount of polyborazole recovered from the pyrolysis has made
extensive examinations difficult. Syntheses now in progress should re-
move any obstacles due to lack of sample.

Elemental analysis of the polyborazoles has been more difficult than
analysis of firing residues because of the presence of volatile compo-
nents. Hydrolysis appears to be the most reasonable route to the deter-
mination of boron. Nitrogen analyses have not been satisfactory and
further investigation on means to get accurate values will be necessary.
The induction furnace method for the determination of total hydrogen has
given one reasonable and two unreasonable results. In fact, all the
values are suspect, since the boron content of the residue is only 30
percent. The similarity of the boron content of the induction furnace
residue and the boron content of an original sample, as found by sodium
carbonate fusion, leads to the conclusion that, in the former as well
as the latter method, some volatile products have escaped. The hydrogen
contained in these volatiles (and it should have been considerable)
was not detected, and the values found represent lower limits for the
hydrogen content. Resolution of this problem will come when the hydride
hydrogen content of the polyborazole is measured.

The differential thermal analysis is quite clear cut. The long endotherm
from 45 to 90 C to 180 to 225 C is the result of the decomposition of
polyborazole to less hydrogenated polyborazoles or BN and hydrogen. The
reaction

$$B_3N_3H_6 \rightarrow 3BN + 3H_2$$
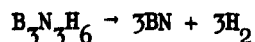
is endothermic, and it is reasonable to take the steps in the over-all
reaction as endothermic. The varying length of time for the decomposi-
tion is a reflection of the sample size, which was not controlled. The
parallelism of the DTA curve with the baseline implies that the rate of
evolution of hydrogen or the ΔH change per mole of hydrogen evolved was
increasing in just the proper proportion as the amount of pyrolyzable
material was decreasing.

The detection of hydrogen atoms in the Knudsen cell of the time-of-flight
mass spectrometer was unexpected. It seems reasonable, however, when
one considers that a B-H bond has a bond energy of only 5 kcal/mole, while
an N-H bond has a 93-kcal/mole bond energy (Ref. 9). It would be expected
that the B-H bond would be easily broken and that the electron of the
resulting free radical would combine with a neighboring molecule to re-
lease another hydrogen atom.

FUTURE WORK

Further syntheses of borazole will be carried out to provide starting material for producing polyborazole. The methods of analysis for boron and nitrogen in the polyborazoles will be developed so that the presence of volatile components will not present difficulties. The route most likely to be successful is an oxygen bomb combustion. Hydride hydrogen will be determined in polyborazole by the gas chromatograph method developed in the last reporting period. Since the gas chromatograph used is the same as the one used in the fluorine analysis, scheduling will have to be arranged.

Mass spectrometric investigations of polyborazole will be of great interest. A high-temperature Knudsen cell is being activated so that components of polyborazole of both high and low volatility may be determined. Polyborazole will be examined on the Mattauch mass spectrometer at AFFTC to yield similar information, as well as to provide a check on the elemental analysis.

Future work will require many samples of firing residues. The motor firings are designed to test mechanical components which have been created to produce maximum performance, i.e., as much BN as possible. These samples, low in BNH solids, are, therefore, less useful for analysis. It is proposed to obtain residues of small motor firings, using components known to produce large quantities of BNH solids. These samples could then be subjected to the methods of analysis developed under the present program. This information would then provide means for correlating analysis of the residues with engine performance. This, however, is beyond the scope of the present program.

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